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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

THE USE OF THE TRANSITION TEMPERATURES OF  
COMPLEX SYSTEMS AS FIXED POINTS IN  
THERMOMETRY.

BY THEODORE WILLIAM RICHARDS AND JESSE BRIGGS CHURCHILL.

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IN a brief paper upon the transition temperature of sodic sulphate,\* we have recently shown that this non-variant point is capable of being reproduced in practice with great certainty, and that it is therefore admirably suited for use as a standard of reference in thermometry. We pointed out the fact that many other systems composed of two or more components might answer equally well, and declared our intention of fixing as many points as possible in order to simplify the accurate measurement of temperature. The subsequent appearance of a hastily written note by Messrs. Meyerhoffer and Saunders,† claiming for themselves a part of this scheme, has prompted the present paper, which has as its object a more detailed statement of the plan.

It is obvious that, while any number of components might be employed simultaneously for this service, the simpler systems will be on the whole the most useful. Water is so omnipresent as to be difficult to exclude from any kind of experiment, hence the investigator is almost forced to adopt it as one of the components. The choice is then of the other material or materials, and the first step was obviously to study all common substances with a view to discover the probable usefulness of the transition temperatures of their aqueous crystals. If a complete temperature scale could not be built up from such simple data it would obviously become necessary to investigate quintuple points, of which a very great number could be devised. This additional complication could not but be regretted, however; for it involves the necessity of preparing two salts instead of one in a pure state, it renders less easy the use of

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\* American Journal of Science, VI. 201 (1898); also Zeitschr. phys. Chem., XXVI. 690.

† Zeitschr. phys. Chem., XXVII. 367, October, 1898.

the same material over and over again, and it introduces a complication which might seriously retard the speed of attaining equilibrium, and hence the constancy of the desired point.

After studying with care the published records of all the field of inorganic chemistry, about two dozen salts were selected as probably suitable for the work in hand. Of these magnesian and nickelous sulphates, calcic and nickelous nitrates, nickelous chloride and borax were rejected as being too inconstant in their indications. The lack of constancy was due sometimes to the smallness of the latent heat of transition, and sometimes to a superabundance of crystalline hydrates. On the other hand, at least eight of the new salts gave results comparable in certainty with those given by the ever trustworthy Glauber's salt. These salts are given in the table below.

TRANSITION TEMPERATURES OF NINE SALTS.

Salt.	By Mercury Thermometer.	By Hydrogen Thermometer.
Sodic Chromate, $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ . .	19.7	19.6
Sodic Sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . . .	32.484	32.379
Sodic Carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . .	35.2	35.1
Sodic Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .	48.1	48.0
Sodic Bromide, $\text{NaBr} \cdot 2\text{H}_2\text{O}$ . . . .	50.8	50.7
Manganous Chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . .	57.9	57.8
Strontic Chloride, $\text{SrCl} \cdot 6\text{H}_2\text{O}$ . . .	61.1	61.0
Sodic Phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ . .	73.5	73.4
Baric Hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . .	78.0	77.9

The temperatures given above are only approximations, and are subject to future revision; at this stage of the work our effort has been only to determine if the points were constant, and not to fix their absolute value. Besides these nine, several other salts promise well. Baric hydrate, given above, was our first trial of three components, for the carbonate was naturally allowed to be present. The study of such quintuple points has now been interrupted by Messrs. Meyerhoffer and Saunders's claim.

These gentlemen studied in a very hasty fashion the transition temperature of Glauber's salt in the presence of an excess of common salt. Although theoretically sound, such a system labors under a serious practical disadvantage; for the addition of heat to it means the dissolving of common salt as well as the melting of crystallized sodic sulphate and the depositing of anhydrous material. The first of these processes is obviously less speedy than the others, and must surely occupy appreciable time even if the solid is finely powdered. Such a "lag" inevitably affects the temperature; our own experience with this mixture as well as with other similar ones supports this inference, and is anything but reassuring. Indeed, we found that Glauber's salt itself did not give absolutely accurate results if it was allowed to "freeze" instead of to "melt," for a similar reason.

We agree with Messrs. Meyerhoffer and Saunders as to the great desirability of uniting upon some normal temperature for the graduating of flasks, etc., but we cannot conclude with them that  $18^{\circ}$  is the best temperature. In America the steam-heated winters and sun-heated summers raise the average temperature of our laboratories at least to  $20^{\circ}$ , and indeed this temperature is more comfortable than  $18^{\circ}$  unless one is performing active manual labor. Hence at Harvard we have settled upon  $20^{\circ}$  as the normal room temperature. Sodic chromate ( $19.6^{\circ}$ ) clearly gives us very nearly the standard of reference which we desire. In determining the specific gravities of liquids, a temperature *above* that of the room is preferable to one *below*, — for the expansion of the liquid during the drying of the exterior of the pycnometer is otherwise apt to be troublesome, hence  $18^{\circ}$  is not suitable for this purpose. The authors before mentioned suggest the use of a bath of mixed salts as a means of keeping the temperature constant during determinations of electrolytic conductivity; but it should be pointed out that in such work the neighborhood of a very large amount of a good electrolyte is necessarily risky, except in the best of hands. This is especially the case when the substance effloresces to form a fine powder, easily wafted around by currents of air. In short, while for some work with closed vessels demanding the greatest accuracy such a bath may be invaluable, the Ostwald thermostat is the safest and most convenient appliance for preserving a constant temperature in the laboratory. The baths of "melting" crystals will find their greatest use in the standardizing of thermometers at fixed points; and these thermometers will continue to serve as the most handy means of attaining and registering any desired temperature. It is obvious that if a thermometer is standardized under exactly the

conditions imposed upon it during its use, the correction for the cool column projecting into the air may be omitted. This correction, by the way, may account for the fact that Meyerhoffer and Saunders found the transition temperature of sodic sulphate to be only  $32.35^{\circ}$  \* instead of  $32.38^{\circ}$ .

We are much pleased that the idea should have been grasped with such eagerness in the laboratory of Professor van't Hoff, for no better proof could be found of its unquestionable utility. We feel too that constants of this sort, like atomic weights, should be studied by more than one set of investigators, and that they should be finally investigated with the utmost care in the Bureau Internationale des Poids et des Mesures, and the Reichsanstalt; hence we are glad to accord to Messrs. Meyerhoffer and Saunders the right which they demand to investigate quintuple points involving sodic sulphate or sodic carbonate. At the same time, we feel that our undoubted priority (our preliminary paper having been finished early in June) allows us to study any desired portion of this field; and for the present, feeling that the simpler systems are the better ones, we shall investigate primarily the salts named above.

CAMBRIDGE, November 14, 1898.

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\* By a clerical error, Rimbach's table for this correction was stated in our last paper to be on page 143 of Landolt and Börnstein's Tables (1894). It is really on page 95.